Rate law I : algebraic method

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

$$\text{rate} = k[A]^{\alpha}[B]^{\beta}$$

- the value of α & β
  - can be any value
  - not related to a & b
  - determined by experiment (or "theory")
- $\alpha + \beta$: order of the Rn
- α : " " with respect to A
- β : " " " " B

Problem : find rate law for the Rn

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$\text{rate} = k[N_2]^{\alpha}[H_2]^{\beta}$$

i.e. find the value of α, β, & k (including units)

based on the below hypothetical experimental data

expt	initial rate	$[N_2]$	$[H_2]$
1	0.2 mM/sec	1 m M	1 m M
2	0.4 mM/sec	1 m M	2 m M
3	0.8 mM/sec	2 m M	1 m M

Steps

1) evaluate the ratio of rates, where there's only one unknown variable
2) repeat for other exponents in the rate law
3) subst into rate law to find k

note: $a\,A + b\,B \rightarrow c\,C + d\,D$

$$\frac{r(1)}{r(2)} = \frac{k[A(1)]^{\alpha}[B]^{\beta}}{k[A(2)]^{\alpha}[B]^{\beta}}$$

$$\frac{r(1)}{r(2)} = \left(\frac{[A(1)]}{[A(2)]}\right)^{\alpha}\left(\frac{[B(1)]}{[B(2)]}\right)^{\beta}$$

i) $\frac{r2}{r1} = \frac{0.4\ mM/sec}{0.2\ mM/sec} = \left(\frac{[N_2(2)]}{[N_2(1)]}\right)^{\alpha}\left(\frac{[H_2(2)]}{[H_2(1)]}\right)^{\beta}$

$$2 = \left(\frac{1\ mM}{1\ mM}\right)^{\alpha}\left(\frac{2\ mM}{1\ mM}\right)^{\beta}$$

$$2 = 2^{\beta}\ ;\ \boxed{\beta = 1}$$

ii) $\frac{r3}{r1} = \frac{0.8\ mM/sec}{0.2\ mM/sec} = \left(\frac{[N_2(3)]}{[N_2(1)]}\right)^{\alpha}\left(\frac{[H_2(3)]}{[H_2(1)]}\right)^{\beta}$

$$4 = \left(\frac{2\,m\,M}{1\,m\,M}\right)^{\alpha} \left(\frac{1\,m\,M}{1\,m\,M}\right)^{\beta}$$

$$4 = 2^{\alpha} \; ; \; \boxed{\alpha = 2}$$

iii) $\text{rate} = k[N_2]^{\alpha}[H_2]^{\beta}$

$$r1 = 0.2 \cdot 10^{-3}\,\frac{M}{sec} = k\,(10^{-3}M)^2(10^{-3}M)$$

$$= k\,10^{-9}M^3$$

$$k = 0.2 \cdot 10^{-3}\,\frac{M}{sec}\;\frac{1}{10^{-9}M^3}$$

$$= \frac{0.2 \cdot 10^{6}}{M^2\,sec}$$

iv) $\boxed{\text{rate} = \frac{0.2 \cdot 10^{6}}{M^2\,sec}[N_2]^2[H_2]}$